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# An Improved Azo Chromophore for Optical NO<sub>2</sub> Sensing

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## *Abstract*

In previous studies, the response to NO<sub>2</sub> of a number of substituted azobenzenes was characterised for sensitivity and kinetics over a range of temperatures. These studies indicated that the optimal sensor of this sort must be based on a chromophore with a binding energy for the target gas of approximately 70 kJ/mol. Here, we present data for the best chromophore which has resulted, dispersed in an addition-cure polysiloxane matrix. We characterise the activation energy for the binding of NO<sub>2</sub> to the azobenzene sites and report measurements of the response time of thin films from which the diffusion constant of NO<sub>2</sub> in the matrix is deduced. We report on the behaviour of the films when operated in the cycled mode. We present quartz-crystal microbalance data allowing absolute calibration of the fractional site occupancy in a related system.

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## INTRODUCTION

There is considerable current interest in the use of organic thin films for the environmental monitoring of gases. For a practical low-cost sensor, measurement of optical film parameters shows a number of advantages over direct electrical measurement [1,2]. In initial studies of such sensors, changes of film refractive index resulting from gas binding were converted into a measurable change of optical intensity by the use of precision microstructures [3, 4]. In recent work, the changes of optical intensity have been mediated directly by the film absorbance [5,6]. We have shown that the latter principle gives a number of technical advantages [7]. The measured quantity is much more directly related to the molecular gas-binding event, leading to considerable enhancement of sensitivity. In particular, dimensional changes with temperature and humidity no longer affect the signal.

We expect the greatest response to be shown by molecules that absorb strongly in the visible region, i.e. chromophores (dyes), and candidates can be found to sense a wide range of gases [8]. We have done most work on NO<sub>2</sub>, and for this gas, azobenzenes have showed the greatest and most specific response [4,9]. It was demonstrated that the gas-binding response of the chromophores can be modelled by a Langmuir isotherm, in which different dye sites behave essentially independently, and each has only two states: vacant and occupied. According to this model, the optical absorbance

$A$  of the film varies linearly with the fractional occupancy  $\theta$  of the dye sites:

$$A = nd \cdot (\sigma_0 + \Delta\sigma \theta) \dots\dots\dots \text{(Equation 1)}$$

where  $nd$  is the areal concentration of chromophore in the film,  $\sigma_0$  is the molecular absorption cross-section of the chromophore and  $\Delta\sigma$  is the change on gas binding.

At a given temperature  $T$ , the fractional occupancy shows the following dependence on the concentration  $c$  of NO<sub>2</sub>:

$$\theta = \frac{c}{c + c_{50\%}(T)} \dots\dots\dots \text{(Equation 2)}$$

Over a small range of temperature, the half-occupancy concentration  $c_{50\%}(T)$  shows essentially Arrhenius-type variation:

$$c_{50\%}(T) = c_{\infty} \cdot \exp(-E_A/kT) \dots\dots\dots \text{(Equation 3)}$$

The activation enthalpy  $E_A$  is the binding energy of the gas molecule to the dye site. In previous purely optical studies, it has proved difficult to determine the absolute value of the fractional occupancy  $\theta$ .

Other behaviours have been reported for different systems. For example, the initial binding event may be followed by a intramolecular rearrangement to a more stable configuration. In some azobenzenes, the stable trans-conformation of the initial molecule switches to cis after a binding event, leading to slow kinetics with more than one time constant. We have demonstrated that this is not the case in our system [10,11]. Another possible complication is displayed by phthalocyanine sensing systems. These often show Elovich kinetics [12,13], indicating substantial intersite interactions, most probably related to the very strong tendency of macrocycles to aggregate face-to-face and thus block their binding sites.

All the chromophores studied so far have shown high temperature dependence of sensitivity. For the most sensitive material reported previously, PS1 (Figure 1(a)), the activation enthalpy  $E_A$  of the optical response is 0.6 eV (60 kJ.mol<sup>-1</sup>) [9]. The resulting variation over commonly encountered fluctuations of ambient temperature is less than ideal for a gas sensor. However the activation energy cannot be decreased arbitrarily, because it has trade-offs with both sensitivity and response time. Whilst lower values of  $E_A$  lead to lower sensitivity variation, they also lead to much lower absolute sensitivity. Conversely, the goal for a practical sensor is not to achieve the highest possible value of  $E_A$ , because higher values slow down the response. If the entropy of activation is small as expected, the Eyring theory of reaction rates [14] predicts a time constant of  $(h/kT)\exp(E_A/kT)$ . For a time constant of 1 s at 290K,  $E_A$  should be 0.735 eV.

These considerations imply that for any practical organic thin film sensor of this type, the temperature must either be monitored or thermostatically controlled. The second option is indicated by measurements of cross-sensitivity to water vapour, which is problematic above 50% relative humidity. The sensor must be operated at a temperature above ambient, and  $E_A$  must be somewhat greater than the 0.6 eV of PS1. We have synthesised a number of derivatives of the original azo compound. Here we present results for the derivative with highest NO<sub>2</sub> affinity. This has two methoxy groups substituted ortho to the azo bridge on the ring already substituted with a donor, as shown in Figure 1.

As stated above, chromophores with high  $E_A$  show slow response combined with high sensitivity, but both response time and magnitude depend on temperature. It is possible to operate these films in a cycled or responsive mode. At ambient temperature, the film integrates the gas concentration. At regular intervals, or in the event of the detection of significant gas binding, which may indicate an acute environmental event or simply continued but acceptably low gas concentrations, a thermostat can be activated to give fast indication of current levels. Finally by heating to a third, even higher, temperature, the bound gas can be driven off and the sensor reset for a further integration phase.

The present aim was to report a thorough characterisation of the new dimethoxy-azobenzene (Figure 1(b)), immobilised both in a polysiloxane matrix and in ultrathin Langmuir-Blodgett films. In addition to optical detection, a quartz crystal microbalance has been used to give an independent measure of the degree of binding of the chromophore.

## EXPERIMENTAL

All the optically-monitored films reported here were fabricated on pre-cut ITO-coated glass slides (200Ω/sq., 10 x 45 x 1 mm<sup>3</sup>, Kendall-Hyde, UK). The polysiloxane mixture deposited on the nonconductive side, and electrodes were attached after film deposition and curing on the ITO side by means of silver-loaded epoxy (Cat. No. 496-265, RS Components, UK). In those experiments requiring thermostating, a T-Type thermocouple (Cat No. 219-4696, RS Components, UK) was

placed in positive contact with the film surface. Both the thermocouple and the ITO contact wires were connected to a switching temperature regulator (Model 2071, 7West, UK).

The test gas mixtures were provided by a computer-controlled mass-flow controller system which has been described previously. The feed gases were:

- dry air
- 100 ppm NO<sub>2</sub> in dry nitrogen

All gases were obtained from BOC (Research grade, UK). Water vapour was added to the air feed line in a bubbler filled with deionised water.

There were two instruments for optical measurement of the ITO slides. In the first, the blue light with peak emission at 430 nm from a light-emitting diode (Cat. No. 264-1386, RS Components, UK) mounted on one side of the slide was detected by a large-area photodiode (Cat. No. 564-021, RS Components, UK) on the other. The second instrument was a UNICAM4 UV/Visible spectrophotometer. In both cases, the slide was mounted in a quartz cuvette provided with two positioning grooves and a well at the bottom to allow unimpeded gas flow down one side of the slide and up the other. The cuvette had a gas-tight lid with a gas inlet, outlet and electrical connections.

For quartz crystal microbalance work, Langmuir-Blodgett films were deposited using a Langmuir trough (Nima System 2030, Coventry, UK) as previously described [10]. The dimethoxy derivative was made up into a spreading solution in chloroform at a concentration of approximately 1 g.dm<sup>-3</sup> and spread onto the subphase of deionised

water with a resistivity of 18 MΩ.cm . Multilayer Langmuir-Blodgett (LB) films were deposited at a surface pressure of 30 mN/m, temperature of 20°C and speed of 33 μm/s.

The LB substrates were AT-cut quartz oscillator crystals with a fundamental frequency of 10 MHz and coated with 50 Å Cr / 1000 Å Au electrodes (International Crystal Manufacturing Co. Inc., Oklahoma City, Oklahoma, USA). After drying in a stream of dry air, the coated crystals were mounted in a custom-built shielded container with gas inlet and outlet lines. They were activated electronically and their frequency measured. The methodology has been described previously [15, 16]. The difference in the fundamental resonance frequency between the clean and coated resonators was used to estimate the mass of the deposited LB layers.

Solutions of dimethoxy azobenzene were made up in toluene (Aldrich, UK, Cat. No. 27, 037-7) together with Sylgard 184, a two-part room-temperature cure polysiloxane manufactured by Dow Corning and purchased from Merck Ltd UK (Cat. No. 634 1655). Table 1 shows the formulations used for films thicker, and thinner, than 100 μm. The less-viscous formulation 2 was used only for the measurements of response time as a function of film thickness. All other measurements were made on films of formulation 1.

Various volumes of solution were spread with a blade over the nonconductive side of the ITO-glass slides. After initial irregularities had evened out, the substrate was transferred to an oven at 110° C for 90-120 min. The film thickness was measured



using a Sloan DekTak contact profilometer across a step cut into the film.

## RESULTS

Figure 2 shows the spectra over the infrared band from 400 – 4000 cm<sup>-1</sup> for a 200 µm-thick film in three different gaseous environments. The control spectrum was taken in dry air, the spectrum marked HCl was taken with a drop of concentrated hydrochloric acid in the cuvette, and the spectrum marked NO<sub>2</sub> was taken in 1% NO<sub>2</sub> in dry nitrogen. Note the change of scale factor of the abscissa above and below 2000 cm<sup>-1</sup>. Many of the peaks of Figure 2 are unaffected by the gas, but there are a number which do vary significantly. In the case of four gas-sensitive peaks, shown in the insets, it was possible to identify a correspondence between the different spectra. In all of these cases the gas shifts the peak to higher wavenumbers, and in all cases the NO<sub>2</sub> shift is slightly more than the shift with HCl, by an average of 30%

Figure 3 shows the absorption spectrum of a film of composition 1 (see Table 1) at three successive stages: before apparent exposure to gas, after exposure to 100 ppm NO<sub>2</sub> at 20°C, and finally after heating to 100° C in the absence of NO<sub>2</sub>. Exposure to NO<sub>2</sub> caused no measurable degradation of response. The subsequent response of the film was equal within experimental error to the initial value. The absorbance of the initial film at the original peak wavelength of 348 nm corresponds to a molecular cross-section for absorption of light of 0.126 Å<sup>2</sup> ( $\epsilon = 7560 \text{ cm}^{-1}\text{mol}^{-1}\text{dm}^3$ ). The absorbance of the gas-treated film at the new peak wavelength of 449 nm corresponds

to a molecular cross-section of  $0.123 \text{ \AA}^2$  ( $\epsilon = 7420 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ ).

The absorbance at 450 nm of the initial film (a) is higher than that (c) after the bound gas has been driven off by heating. This fact can be explained by the presence of NO<sub>2</sub> in the laboratory ambient at low concentrations. On subsequent exposure-reheating cycles, the absorption recovers to curve (c). For all films investigated, spectra taken at different concentrations showed a distinct isosbestic point near 370 nm, indicating that only two species are involved.

Figure 4 shows typical measurements of the optical absorbance at 430 nm versus temperature at three different gas concentrations. The continuous curves show the best fit to a Langmuir isotherm model. The best fit binding energy was found to be 0.73 eV.

Figure 5 shows the time behaviour of the films with cycling of the NO<sub>2</sub> concentration and temperature. Gas was pumped continuously across the film cell, but the NO<sub>2</sub> concentration was switched between 0 and 100 ppm as shown by the [NO<sub>2</sub>] line. Similarly the temperature of the film was switched between 25°C and 60°C as shown by the T/°C line, giving four phases which may be symbolised 1, 0A, 2 and 0B, respectively. Of particular note is the slight “rebound” during phase 0B as the film temperature drops. All aspects of this rebound have been found to be consistent with the recapture by the chromophores of NO<sub>2</sub> released from them into the matrix before it has diffused out of the film.

The kinetics during phases 1 and 0A can be fitted to an exponential curve and the time constant for the sensor response determined. The variation of time constant with film thickness is shown in Figure 6 plotted on a log-log scale. The straight line gives the best fit to the square-law dependence (log-log gradient 2) to be expected if diffusion through the film is the dominant factor determining response time. The fit is satisfactory, and there is very little indication of a transition to a thickness-independent regime where other factors dominate, e.g. molecular binding kinetics.

Figure 7 shows the response to temperature of a newly fabricated film unexposed to gas. In a run over a period of 136 mins with a film immersed in pure dry N<sub>2</sub> at 25°C, the maximum variation was equal to that produced by a concentration of 91 ppb of NO<sub>2</sub>.

Figure 8 illustrates the use of the QCM to monitor absorption from an air stream containing 100 ppm NO<sub>2</sub>. Crystals coated with a varying number of LB layers were used and, as expected, the total frequency change after equilibrium was established depended on the number of layers and hence on the total number of chromophores present in the coatings. QCM results are normally interpreted using the Sauerbrey equation [17] to relate the linear change in frequency  $\Delta f$  due to an increase in mass, M:

$$\Delta f = \frac{f_0^2}{AN\rho_0} \cdot M \quad \dots\dots\dots \text{(Equation 4)}$$

where  $f_0$  is the fundamental oscillation frequency of the quartz crystal,  $A$  is the active area of the gold electrode,  $N$  is a constant for the particular grade

of quartz and  $\rho_Q$  is the density of quartz. While it is well known that Equation 4 is at best an approximation, it is adequate [18] so long as the frequency change is limited to  $|\Delta f| < 0.02f_0$ . In spite of the much lower film thickness, the response times shown in Figure 8 are considerably slower than in the optically-monitored polysiloxane-matrix films, indicating the much lower permeability of the well-ordered LB system.

The fractional occupancy of gas-binding sites for LB films of three different thicknesses is shown in Figure 9. The error bars were deduced by making a number of measurements on each film. The near-constancy of  $\theta$  indicates that the quantity absorbed is not limited by diffusion through the layers.

## DISCUSSION

In the infrared spectra of Figure 2, the gas-sensitive peak near 810 cm<sup>-1</sup> is attributable to the azo bridge [19]. Another azo peak is expected in the vicinity of 1220 cm<sup>-1</sup>, but there are many candidate peaks and their correspondence between the three spectra is not clear. The similarity of the effects on the infrared spectrum of both NO<sub>2</sub> and HCl indicate the same binding site for both gases, which must clearly be a lone pair of one of the nitrogens of the azo bridge. This is also consistent with the pattern of gas sensitivity shown by molecules of similar but systematically varied structure. These results have already been reported [10].

The 0.73 eV gas-binding energy of the dimethoxy chromophore determined from the

dependence of the response on temperature is 20% higher than the value of 0.6 eV determined for the original chromophore PS1. The increase correlates as expected with the increased film sensitivity [9]. Since the measured response time is dominated by diffusion through the film matrix, it has not proved possible to confirm the expected dependence on temperature of the molecular binding kinetics.

Figure 5 provides information on the behaviour to be expected in applications where a thermostat is activated periodically. During phase 1 the film temperature is low and the NO<sub>2</sub> concentration high. The film absorbs gas with quite a long time constant. In phase 0A the heater and the NO<sub>2</sub> are both off and the response decays only slowly. At the beginning of phase 2 the increase in temperature causes a marked reduction in time constant just as previously reported for films of PS1. The signal decays rapidly to zero. In order fully to “reset” the sensor response for subsequent operation in a low-temperature integration mode, the heating cycle must last for a period significantly longer than the response time at the raised temperature.

In Figure 6, the data points show significant scatter related to experimental difficulties, but give a reasonable fit to a square-law dependence with layer thickness  $d$  over an order of magnitude of time response  $\tau$ . There is no sign of a transition to a thickness-independent regime, indicating that the response time is dominated by diffusion through the polysiloxane matrix. From the present data, the diffusion constant for NO<sub>2</sub> in the polysiloxane matrix at 25°C is estimated from the formula:

$$D = \frac{4d^2}{\pi^2\tau}$$

to be  $100 \mu\text{m}^2.\text{s}^{-1}$ . This value is 3 orders of magnitude lower than values reported for chemically inert gases through comparable polysiloxanes [20]. Because of the dominance of diffusion, it has been impossible to determine the precise intrinsic molecular response time, but it must be less than 10 s at 25°C, consistent with the Eyring theory prediction.

It is of interest that the response time of PS1 films was also dominated by diffusion through the matrix, demonstrated by the distinct values for the activation energies of response time and sensitivity [9]. This suggested that the NO<sub>2</sub> also interacts chemically with the polysiloxane matrix, although with only half the energy of its binding to the azobenzene, resulting in a gas concentration  $c$  in the matrix considerably higher than in the adjacent air. The storage of a considerable amount of gas in the matrix is consistent with the rebound phenomenon apparent in Figure 5. The quantity which is constant across the air-film interface is the partial pressure,  $p$ , which is usually related to the concentration by Henry's law  $c = Hp$ .

Recent studies of diffusion through thin polysiloxane membranes [21] have reported, not the diffusion constant  $D$ , but the product  $DH$ , called the permeability, unfortunately only for gases inert to polysiloxane. In future work we intend to quantify the Henry coefficient  $H$  for chemically-active gases and to make the link to the response time activation energy.

The sensitivity of a gas sensor is the concentration which gives a signal equal to the peak fluctuation from other causes. Temperature fluctuations most probably mediated by changes of chromophore environment are one possible cause. Referencing the gradient of Figure 7 to gas concentration, the sensitivity is 210 ppb/K at 25°C. The measured value of 91 ppb for fluctuations of a film thermostatted to 25°C is consistent with the temperature drift expected from the thermostat, so it is probable that even better sensitivity is achievable.

The linear relation of frequency change to mass allows the estimation of the fraction of chromophore sites that interact when the absorption reaches equilibrium. From the data shown in Figure 9 and assuming a 1:1 interaction between NO<sub>2</sub> and a dye molecule, the values shown in Table 2 were calculated. There is no significant variation of the result with layer thickness for those studied here.

The quartz crystal microbalance data provides an absolute value for the fractional occupation  $\theta$  of chromophores by the analyte gas. It can be seen that the dimethoxy chromophore sites are just less than half occupied at 100 ppm concentration and 25°C. Because of the difference of molecular environment, these values are not directly transferrable to the case of chromophores in a polysiloxane film.

## CONCLUSION

By appropriate substitution, the energy of binding of NO<sub>2</sub> to the basic PS1 chromophore reported previously has been increased by 20%. The intrinsic response

time of the enhanced chromophore at 25°C is still less than 10 s and below the threshold measurable with our equipment. The sensitivity of the new material to NO<sub>2</sub> has been demonstrated to be better than 100 ppb at 25°C when interrogated appropriately. The feasibility of cyclic thermostatted operation has been shown.

In much early work on optically interrogated gas sensors, the propagation phase shift (which is defined by the real component of film polarisability) was converted to measurable changes of optical intensity using precision optical microstructures. The present study confirms that the propagation loss or absorption (defined by the imaginary component of polarisability) is much more directly measurable and dispenses with the requirement for precision fabrication. In addition to simpler manufacturing protocols the new interrogation principle inherently gives better linearity with gas concentration and is unaffected by processes leading to dimensional change, e.g. chemical degradation, mechanical creep, uptake of moisture and other substances, etc.

The sensor output depends on the amount of analyte gas bound to chromophores. Analyte gas is additionally present in the films loosely bound to the polysiloxane matrix. Down to the lowest temperatures investigated the sensor kinetics are dominated by the diffusion of the gas in the matrix, and the diffusion coefficient has been found to be  $100 \mu\text{m}^2\cdot\text{s}^{-1}$  at 25°C. Intrinsic molecular response times are expected to be reached for film thicknesses less than 10  $\mu\text{m}$ .



## Acknowledgements

One of us (AB) thanks the EPSRC for a postdoctoral grant. We thank Kidde International for continued interest and support in kind. Thanks are due to Dr J. Scheerder for the synthesis of the active materials, to Mr J. Lovering and Mr A. Cranston for assistance with sample preparation and to Mr M. Taylor for assistance with electronic equipment. Financial support of the QCM work from the University of Bath is gratefully acknowledged.

## List of Captions

Table 1. Compositions of the solutions used for spread-coated films

Table 2. Measured frequency shifts of a quartz crystal on deposition of LB overlayers and subsequent exposure to 100 ppm NO<sub>2</sub> in an inert carrier gas; calculated values of the absolute fractional occupancy of azobenzene sites.

Figure 1. Molecular structures (a) of the previous best chromophore PS1 and (b) of the derivative investigated here with two methoxy groups ortho to the azo bridge on the “upper” ring.

Figure 2. Infrared spectra of a 200 µm-thick film (a) not exposed to gas (b) exposed to 1% NO<sub>2</sub> and (c) exposed to HCl vapour. Note the change of scale below 2000 cm<sup>-1</sup>.

Figure 3. UV/visible absorbance spectra of films of composition 1 (a) before exposure to NO<sub>2</sub> (b) after 30 minutes exposure to 100 ppm NO<sub>2</sub> at 25°C (c) after heating to 100°C for 10 minutes in the absence of NO<sub>2</sub>.

Figure 4. Typical measurements of absorbance response with temperature at three different NO<sub>2</sub> concentrations (a) 75 ppm (b) 50 ppm (c) 25 ppm. The curves show the best fit to a Langmuir isotherm model with binding energy 0.73 eV.

Figure 5. Temperature-concentration cycle of gas response using the 430nm light-emitting diode rig.

Figure 6. Log-log plot as a function of film thickness of the time response of the films to 100 ppm NO<sub>2</sub> at 25°C.

Figure 7. Response to temperature of a newly fabricated film unexposed to gas

Figure 8. Response of QCM to 100 ppm NO<sub>2</sub> in air. The arrow indicates the time at which NO<sub>2</sub> was admitted.

Figure 9. Fractional occupation of NO<sub>2</sub> binding sites in equilibrium with 100 ppm NO<sub>2</sub> at 25°C for LB films of three different thicknesses.

Equation 1. Dependence of absorbance on fractional occupancy

Equation 2. Dependence of fractional occupancy on NO<sub>2</sub> concentration.

Equation 3. Dependence of half-occupancy concentration on temperature

Equation 4. Sauerbrey equation

## TABLES

Formu- lation	Thickness range ( $\mu\text{m}$ )	Dimethoxy azobenzene (moles)	Sylgard 184A Polysiloxane (g)	Sylgard 184B Curing agent (ml)	Toluene (ml)
<b>1</b>	>100	0.002	3.00	0.5	2.00
<b>2</b>	<100	0.004	3.00	0.5	4.00

Table 1. Compositions of the solutions used for spread-coated films of thickness greater than, and less than, 100  $\mu\text{m}$ .

LB Films	Deposited Azo dye	NO <sub>2</sub> gas interactions	Occupancy
No. of layers	$\Delta f$ (Hz)	$\Delta f$ (Hz)	$\theta$
20	1382	55	0.445
30	2116	87	0.4309

Table 2. Measured frequency shifts of a quartz crystal on deposition of LB overlayers and subsequent exposure to 100 ppm NO<sub>2</sub> in an inert carrier gas

## FIGURES

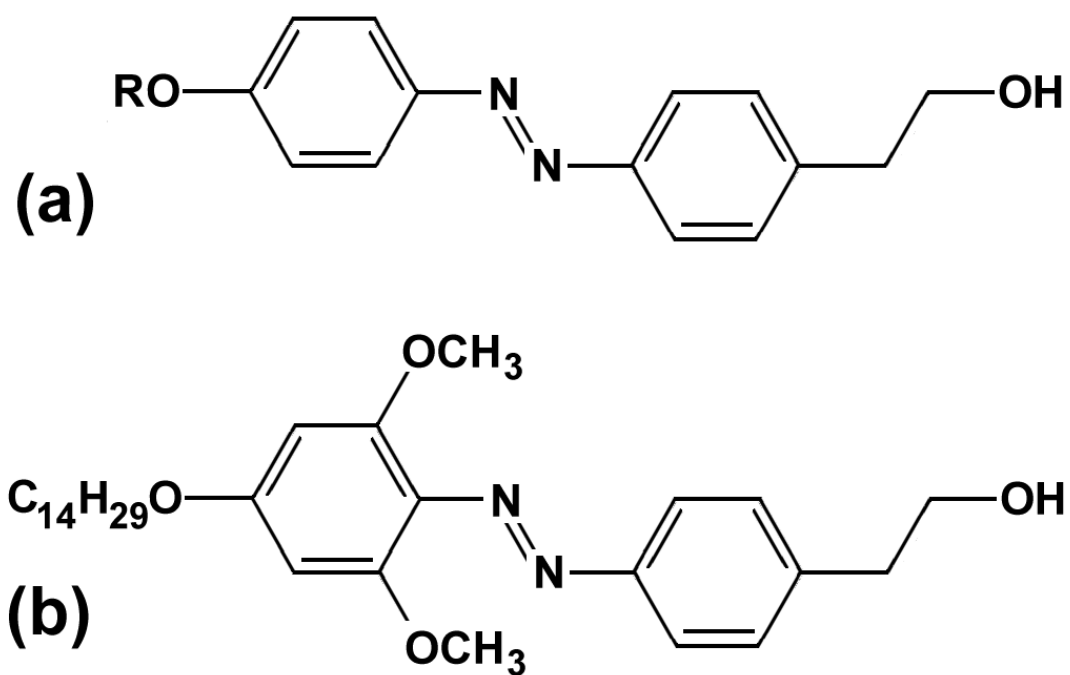


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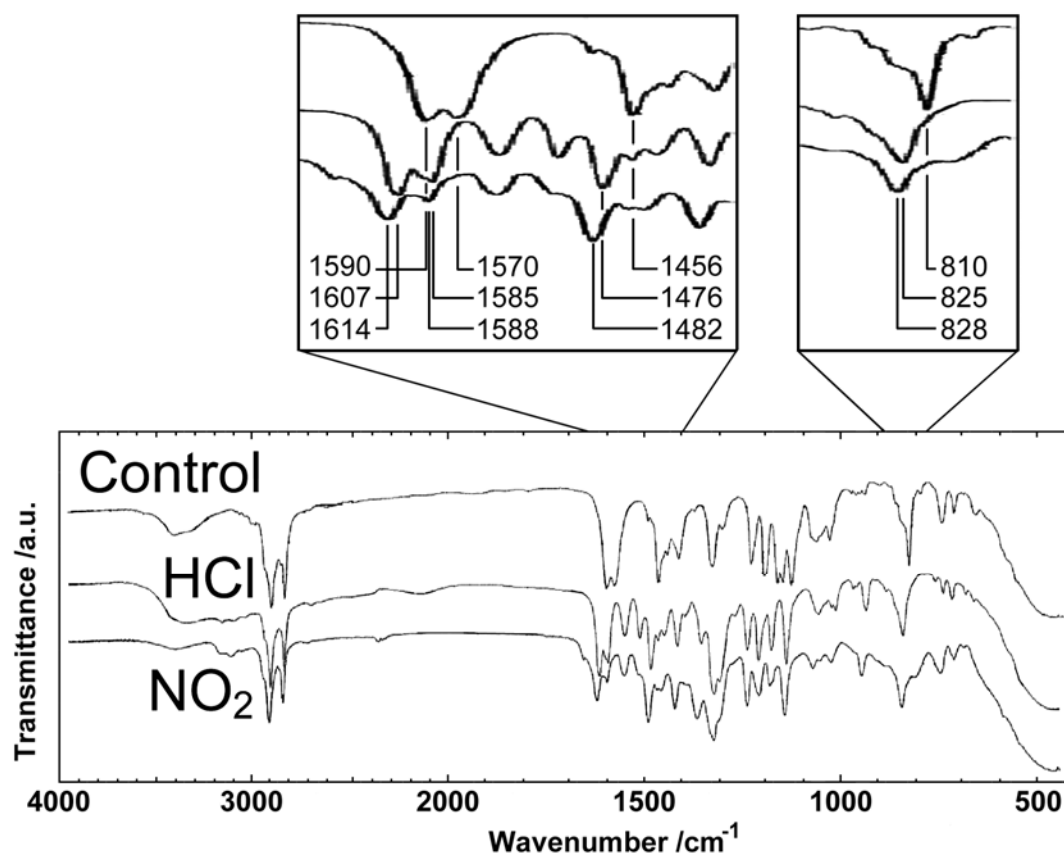


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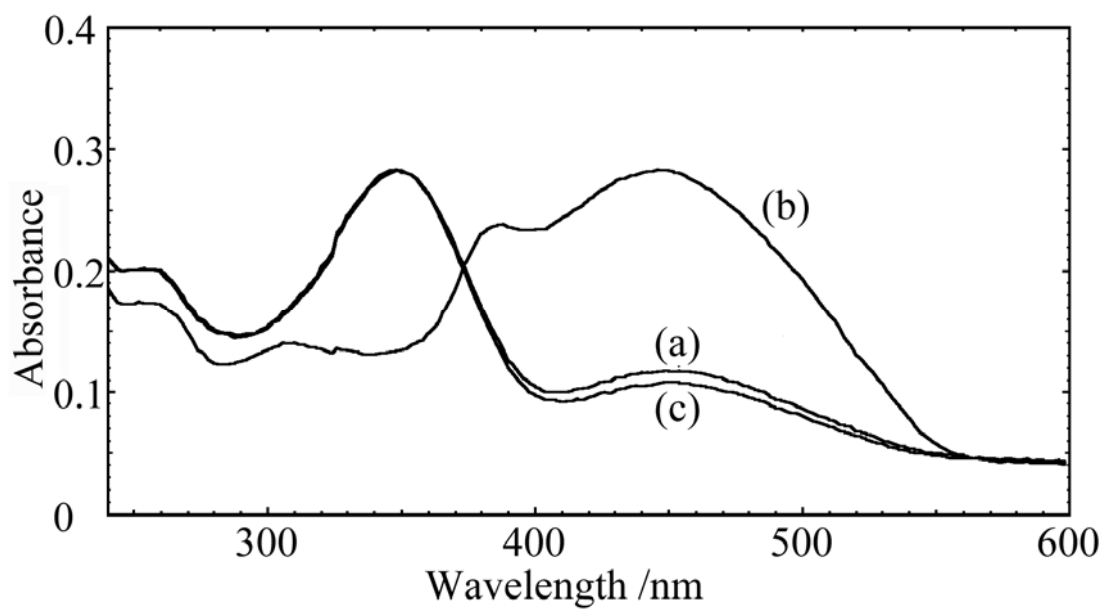


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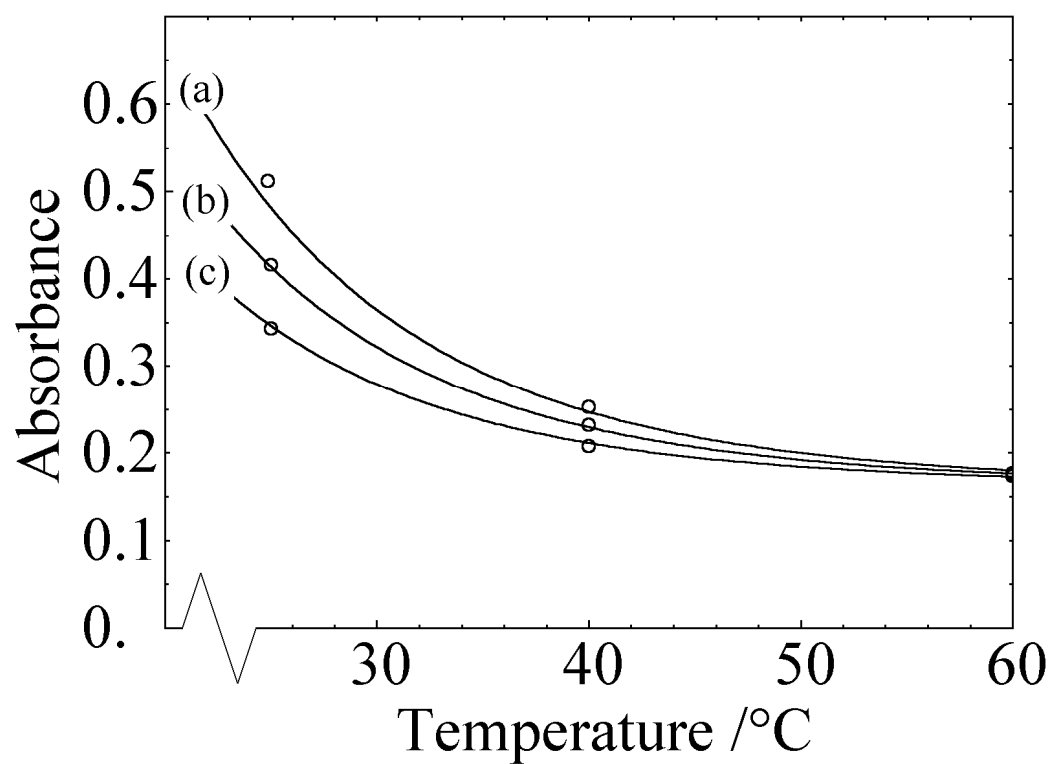


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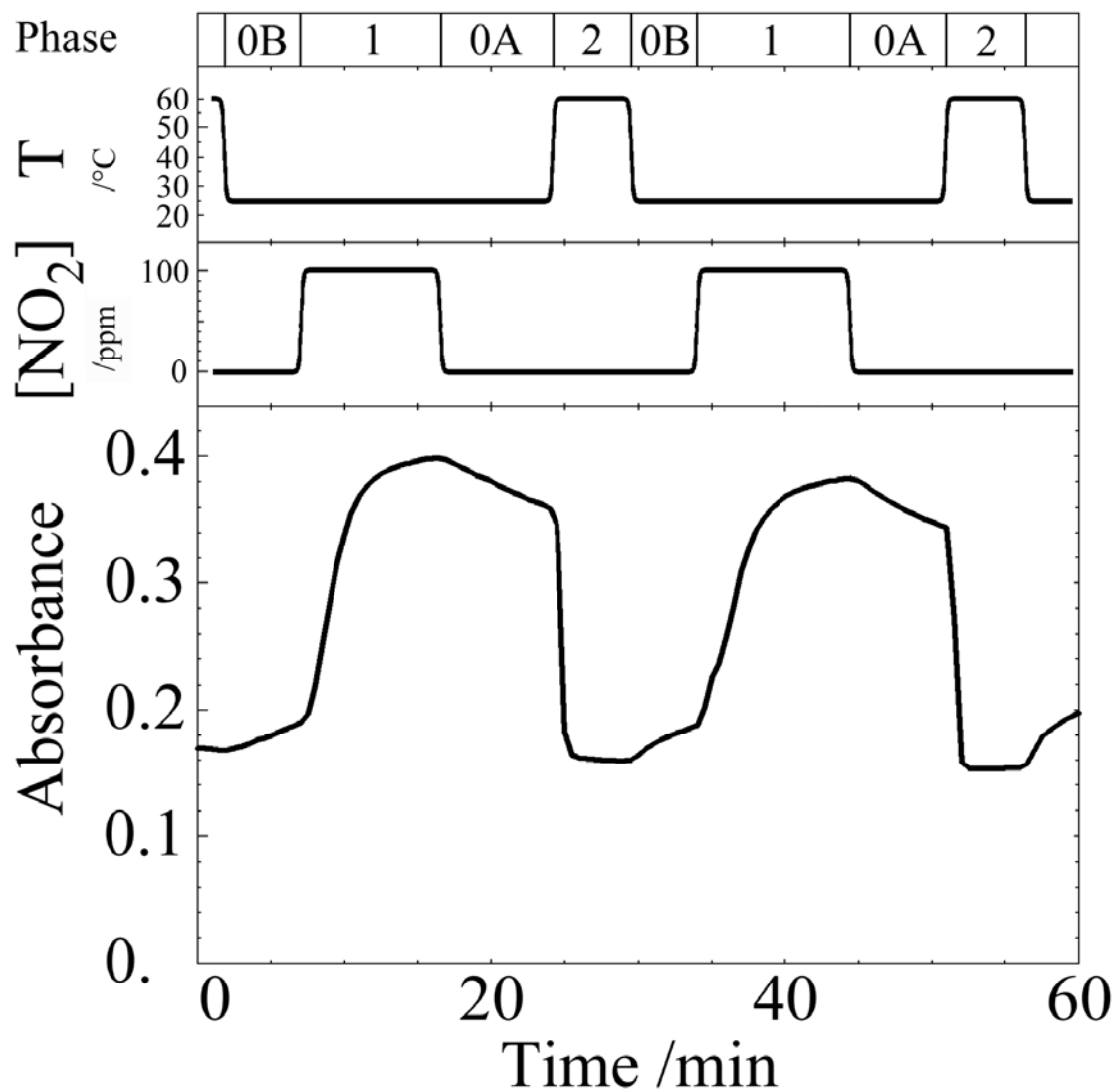


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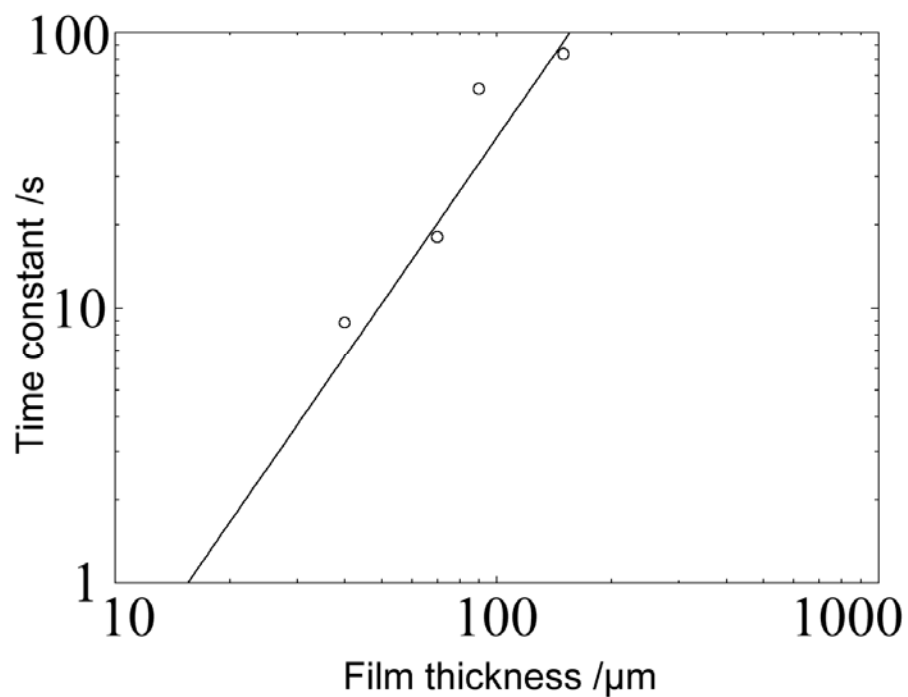


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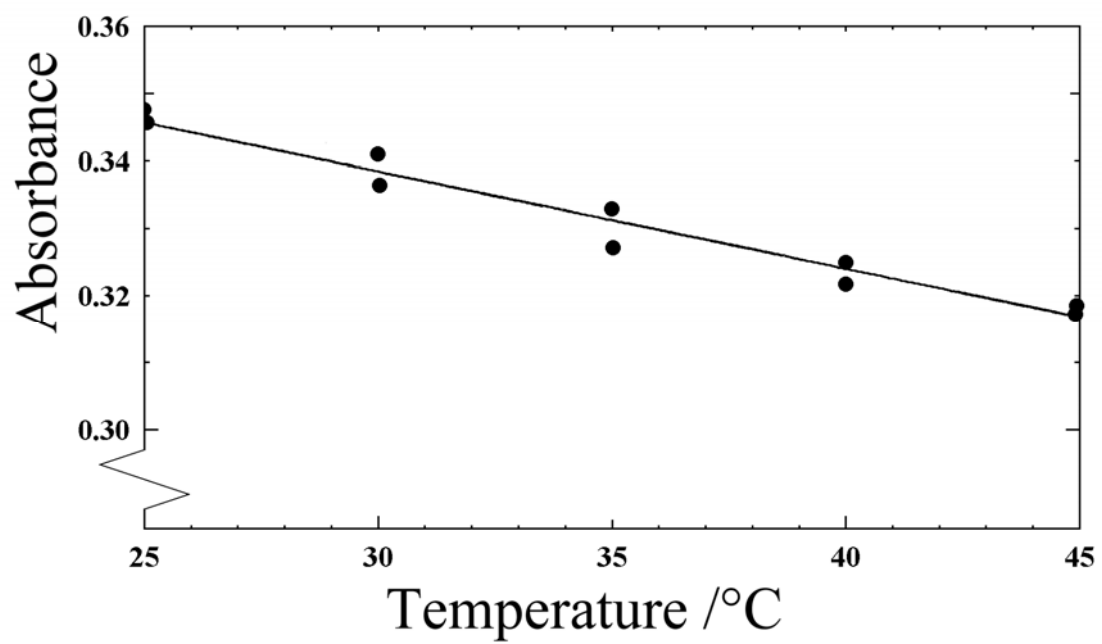


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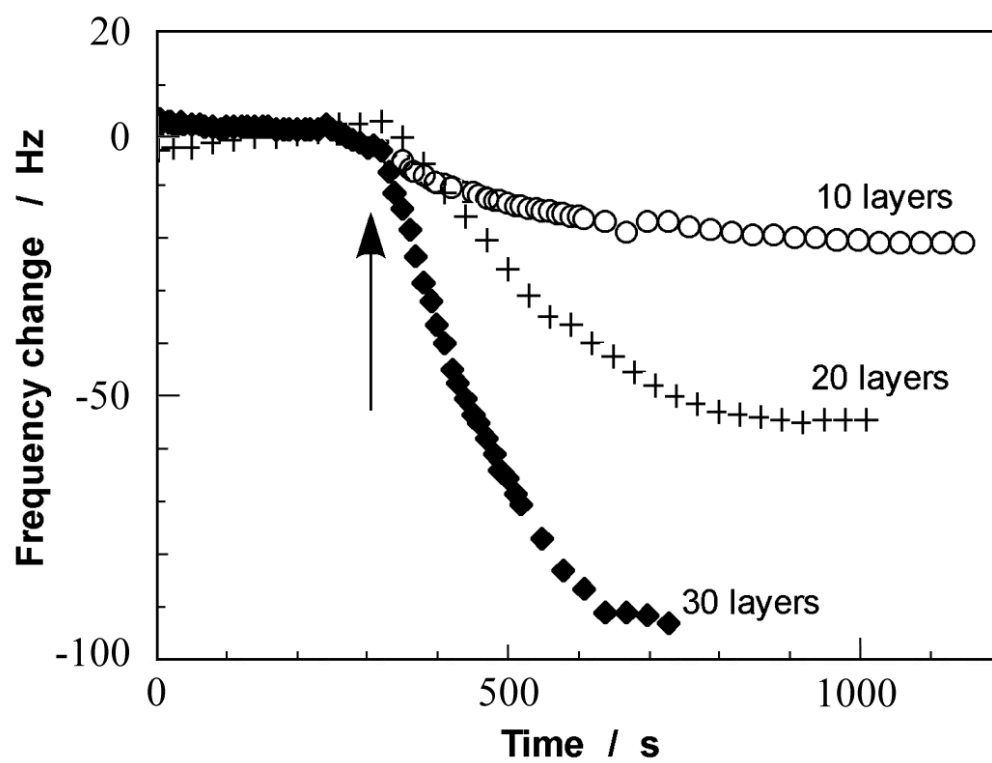


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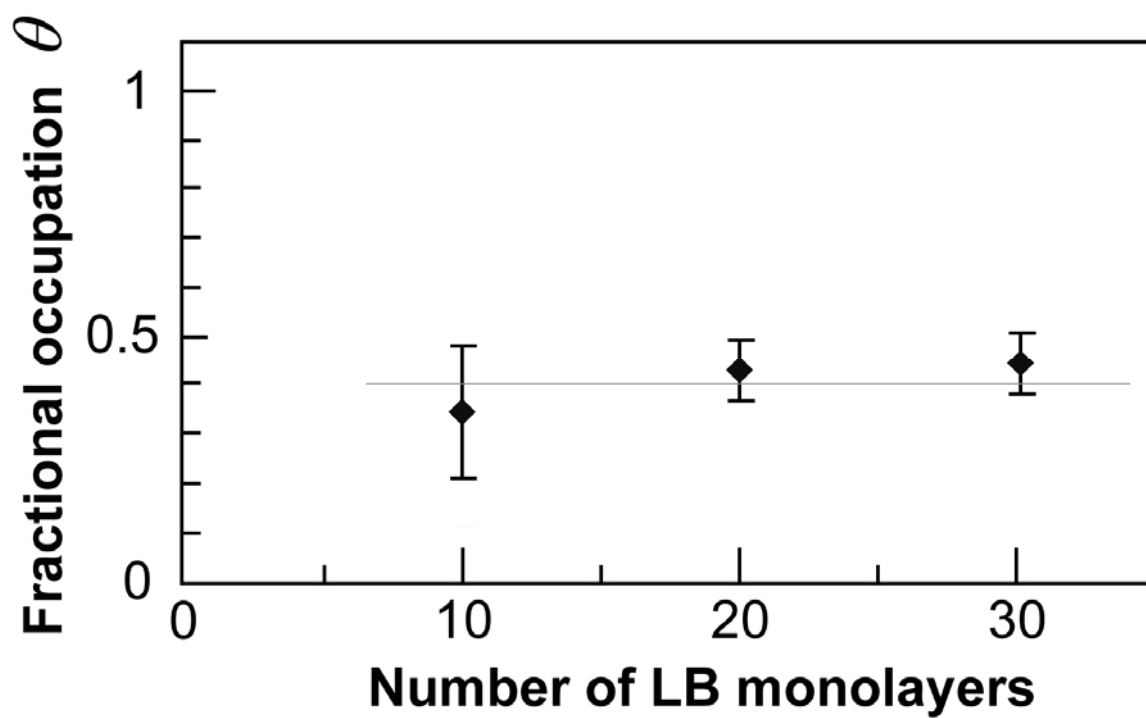


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